Energy research hots up

Accused of damaging the environment, current techniques for producing energy will make way for new energy technologies. Cause for intense activity in research laboratories.

>>> Stéphan ASTIER, professor at INPT, a researcher at LAPLACE (joint UPS/CNRS/INP laboratory) and Maurice Comtat, professor at UPS, a researcher at LGC (joint UPS/CNRS/INP laboratory)

LAPLACE: Laboratoire Plasma et Conversion d'Energie/Laboratory on Plasma and Conversion of Energy

CIRIMAT: Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux/Interuniversity Research and Engineering Centre on Materials

LGC: Laboratoire de Génie Chimique/ Chemical Engineering Laboratory

Energy accounts for 50% of mankind's ecological footprint. Even electricity, an energy vector that has many qualities justifying its continued development, produces up to 35% of the anthropogenic emissions of CO_2, placing it top of the list of greenhouse effect gas emitters!

The primary objectives set by the European Union are described by the "three times 20 for 2020" concept: 20% reduction in consumption, 20% reduction in CO_2 emissions and 20% increase in renewable energies. But the latter provides power with large daily and seasonal variations, often in the form of an intermittent production of electricity that can affect the stability of an entire grid. This means renewable electricity, which requires new storage methods, must be made more attractive. This is particularly the case for wind generators and photovoltaic plants, which are very promising. Moreover, considering the strong development of autonomous electronic systems, used for many mobile or portable applications separated from the grid, new energy storage needs, notably electricity storage, have emerged and have become crucial in new energy technologies.

Batteries

Electrochemical batteries are an efficient way to store and deliver electric power, in a reversible or irreversible manner. These batteries have been improved over recent years using nickel metal hydride and lithium technologies, both in "energy" or "power" versions. Rechargeable or not, they represent a considerable market that is growing well. But the problem is that they still offer much lower performance than fuel systems. Not only do they have a much lower energy capacity but also a much more "damaging" power density that significantly lengthens the amount of time it takes to recharge the battery. In contrast, chemical energy storage using fuels offers both high performance in terms of specific energy to mass and volume and a variety of other benefits, such as convenient transport. This is a major advantage of fossil fuels and something that is difficult to find with other sources and carriers.

Hydrogen

Analysis indicates that it would be wise and useful to move from a situation dominated by fossil fuels, which satisfy the dual function of energy sources and carriers, to a situation exploiting other energy carriers, which have comparable qualities with added advantages. For example, these alternative carriers should be easy to store and transport, not contain fossil carbon, promote the development of non-CO_2-emitting sources and be renewable. Among the many possibilities is the electricity-hydrogen combination, two energy carriers with complementary properties. They are interconvertible through clean and efficient electrochemical processes, involving electrolysers and fuel cells in particular.

The following papers present some of the research work being undertaken in research laboratories in Toulouse that aims to contribute to the "three times 20 for 2020" goal. We begin by discussing the use of molten salts for the next new generation of nuclear reactors. These will help France continue to produce electricity from nuclear power (80% of the total energy production) with low CO_2 emissions. Some future reactors will specifically produce hydrogen from water for heat and electricity.

Next, we present low or high temperature fuel cells, using hydrogen fuel, which is very promising for generating electricity and heat.

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headline

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Hydrogen is the subject of intense research, from electrode materials to complete operating systems. This is also the case for supercapacitors, new electrochemical devices enabling rapid storage and delivering electrical energy -- true "boosters" for electrical systems.

As for hybrid systems, they cleverly combine sources and storage devices in complex architectures that operate in many new systems in order to improve overall energy efficiency. Finally, we talk about new lighting technologies that allow significant reductions in electricity consumption.

These few examples show the great variety of research activities being undertaken at Toulouse in the field of energy, a tradition that dates back to the 1920s when the Faculty used to deliver the diploma of electrochemical engineering under the auspices of Dean Paul Sabatier. It is important to note that electrochemical processes and components occupy a prominent place among these new energy technologies developed to build a new sustainable energy landscape.

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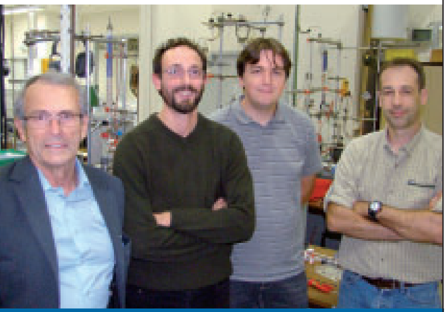
The school programs:

Among the school programs related to the theme "energy" at UPS, we especially highlight the Erasmus Mundus Master "Materials for Energy Storage and Conversion". This two-year program involves five universities in three European countries (France, Poland, Spain) that host several internationally reputable laboratories in the field of materials for energy.

For more information: **http://www.u-picardie.fr/mundus_MESC/**

The Molten Salt Reactor: nuclear energy for the future

The world's demand for energy is on the increase but we need to reduce greenhouse gas emissions. Could new nuclear reactor concepts be the answer?



>>> Pierre TAXIL, professor at UPS; Laurent CASSAYRE, CNRS research scientist, Laurent MASSOT, assistant professor at UPS and Pierre CHAMELOT, assistant professor at UPS. Electrochemical Processes in Molten Salt team at the Laboratoire de Génie Chimique LGC (joint UPS/CNRS/INP laboratory).

Nuclear energy that is safe, competitive, without proliferation risks, sustainable, and which produces a minimum amount of waste. An utopia? No, this is actually the goal of the Generation IV International Forum (GIF), which, since 2000, regroups several countries (including France) and the European Community (since 2003), in an attempt to find new nuclear reactor concepts fulfilling these requirements before 2040.

To this end, the GIF has selected six so-called Generation IV reactor concepts. Among them, the molten salt reactor (MSR), which contains a liquid core made up of a molten alkaline fluoride salt (for example, LiF-NaF) with dissolved fuel at a temperature of around 500°C.

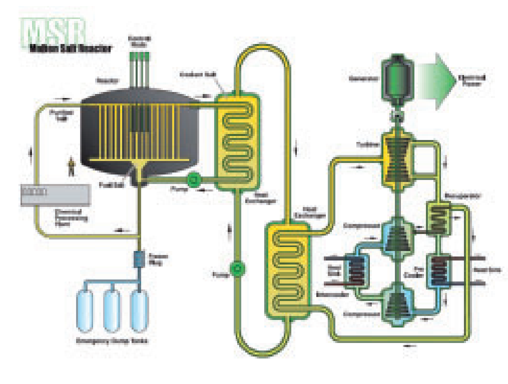
Its advantages: it is simple to prepare and transport the fuel as well as limit radioactive waste production. MSR could also run with the thorium cycle (replacing UF_4 by ThF_4 in the molten salt), an advantage since estimated reserves of Th are four times higher than those of U.

Today, two key points have to be assessed to ensure that this concept is indeed an interesting one: the on-line molten salt reprocessing unit and the availability of structural materials sufficiently resistant to the highly corrosive salt environment.

Based on knowledge developed over thirty years in the field of molten salt processes, our team is now working with national (CNRS-PACEN) and European (ALISIA) research programs. In the last five years, we have performed various experimental studies dealing with separation processes relevant to molten salt reprocessing.

Molten salt reprocessing

The physico-chemical behaviour of thorium and some fission products (particularly the lanthanides) has been studied in molten media in an attempt to bring our understanding of this subject up to date. We have determined redox potentials, oxidation states in solution and compound stabilities using several electrochemical techniques as a function of various parameters, such as temperature, salt composition and oxygen content. This data makes up a helpful base to establish a global reprocessing scheme for the salt. In particular, it highlights the importance of oxide compounds in the salt. These oxides are responsible for a partial precipitation of the fuel, which is a drawback for MSR performance.



>>> Molten salt reactor concept

Lanthanides make up part of the fission products issued from nuclear reactions. Due to their strong neutron absorption properties, we must remove them from the molten salt in order to ensure efficient reactor operation. To extract lanthanides, several processes are being studied in our laboratory: selective precipitation by oxide addition and electrolytic extraction on various cathode substrates (inert, reactive or liquid). The best extraction efficiencies (above 99.6%) have been obtained thanks to an original electrolysis process using a so-called reactive nickel cathode that forms intermetallic compounds.

Corrosion resistance

Hastelloy-type (Ni based) metallic alloys are also being studied in our laboratory in order to determine their resistance to corrosion in several molten fluoride media and to optimize their composition. We use classical electrochemical techniques on immersed probes in molten salts coupled with ex-situ material characterisations. In particular, we have shown that the chromium contained in Hastelloy does not offer protection because of its solubility in the molten salt, in contrast to what is observed in air where a protective chromium oxide scale forms.

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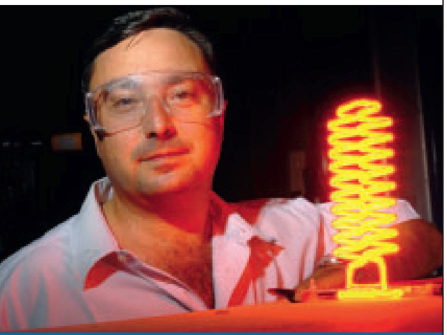
A revolution in public lighting

Lighting consumes a fifth of the world's electricity. It is thus extremely important to develop new more efficient light sources. This is the challenge undertaken by a laboratory in Toulouse.



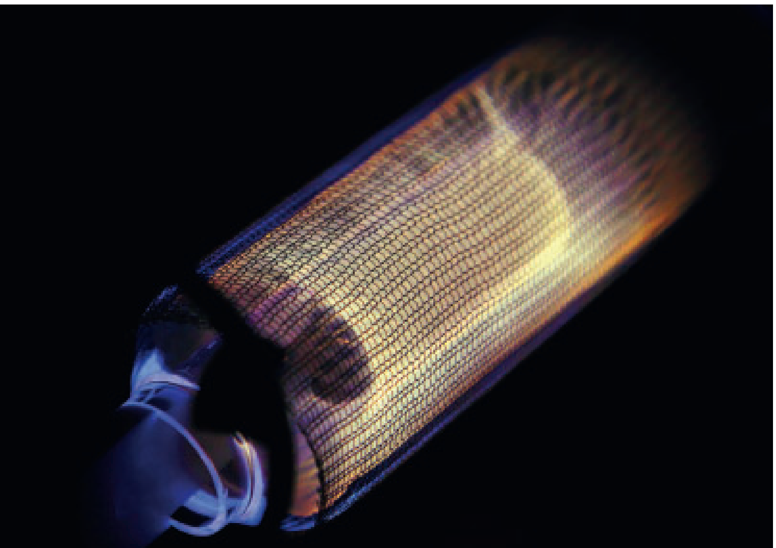
>>> Georges ZISSIS, professor (UPS), researcher at LAPLACE (joint UPS/CNRS/INP laboratory)

Electric lighting has radically changed our daily lives, allowing us to work and play for longer hours and it is impossible to imagine the developed world without artificial lighting. An estimated 30 billion electric lamps are in use on the planet, and 10 billion new lamps are produced each year. The amounts of energy consumed are phenomenal and world consumption of electricity for lighting is as high as 2650 TWh per year. This is roughly 19% of total electrical generation worldwide. More worryingly, this electricity consumption corresponds to 1700 million metric tonnes of CO_2 being released every year.

Finding new ways to light lamps is a scientific, technological, economic and environmental challenge.. After increasing steadily over the last 75 years, electric energy conversion efficiency by commercial light sources appears to have reached a plateau of about 33% of the theoretical maximum at 100-110 lm/W. But, the theoretical maximum for white light production could be as high as 300 lm/W.

Spectacular progress

A revolution in the domain of light source technologies is on the way today: High Brightness Light Emitting Diodes are arriving on the market of general lighting; Organic LEDs (OLEDs) have seen spectacular advances and a new generation of electrical discharge based on molecular radiators has become reality. Novel light sources might therefore rapidly reach 200 lm/W. Replacing old technologies by new lamps may lead to energy savings on the order of one billion oil barrels (which corresponds to a global production capacity reduction equivalent to more than 250 large electrical power plants).



>>> Dielectric Barrier Discharge lamp produced at LAPLACE. This lamp uses a novel concept for light generation: molecular radiators, which might even be the next generation of light sources.

A better understanding of the fundamentals of electrical light source operation will allow an optimization that could compensate for the increase in the demand for light. The very first objective is to enhance the luminous efficacy (increase the light flux per electrical watt consumed by the lamp) and then enhance the colour rendering (the light should reproduce high fidelity natural colours).

The Laboratoire Plasma et Conversion d'Energie (LAPLACE) has played a very important role in the domain of the science and technology of light sources for more than 30 years now. The research group "Lumière et Matière" (Light and Matter), today made up of 15 staff members, was at the origin of the "Efficient Lighting for the 21st Century" European network. This Network brought together more than 70 institutions from 20 European countries during 5 years. Furthermore, several European projects have been initiated and coordinated by this research group.

Albi city lighting system

An example is the NumeLiTe project that demonstrated a street lighting system in downtown Albi. LAPLACE's contribution to the project was decisive because the developed research led to the creation of new ceramic metal halide lamps able to produce light with a luminous efficacy of 100 lumens/W and with a life span of more than 16000 h. Today these lamps, produced by one of the industrial project partners, are commercially available worldwide. Moreover, the research was rewarded with the prestigious 1st prize of the International Electrotechnics Committee (IEC) centenary challenge in 2007. Today, LAPLACE is still working in close collaboration with major industrial actors for the development of a new generation of light sources using molecular radiators (Dielectric Barrier Discharge Lamps) and OLEDS.

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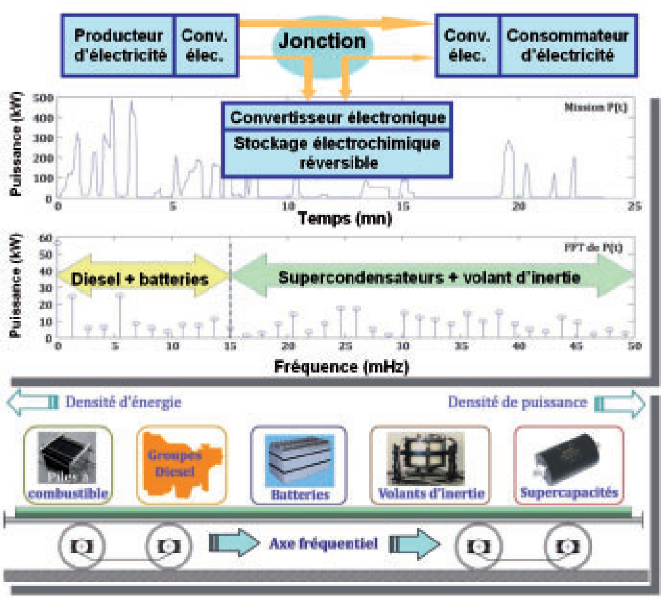
Hybrid energy systems

Recovering the energy lost in internal combustion engine motors by optimizing their operation is not the prerogative of hybrid cars. A review of applications studies undertaken at LAPLACE.

>>> Stéphan ASTIER, professor at INPT, researcher at LAPLACE (joint UPS/CNRS/INP laboratory)

Hybridization: the word rightly evokes so-called hybrid vehicles, involving both electric and internal combustion engines. These electric vehicles carry an on-board electric generator capable of recharging its electrochemical batteries. But in the current energy context, hybridization must be considered in a much broader sense as illustrated by studies conducted at LAPLACE, within the research group "ENESYS" (Electric ENergy and SYStemic). Indeed, it concerns many systems exploiting "New Energy Technologies" components, such as renewable sources, fuel cells, electrolyzers and batteries that can be judiciously implemented in complex hybrid architectures that need to be designed and optimized.
From an elementary point of view, we can assume that hybridization consists of introducing a reversible energy storage system between consumers and producers of electricity. This introduces a decoupling and degrees of freedom that allow optimized management of energy flows within the system.
The interconnection of these units is done through electronic static power converters, and architectures are very varied. The attached figure illustrates a basic hybrid junction for three sources. In this example, the flow of energy options is indicated considering the usual case of a generator supplying a reversible load that the storage system can take advantage of (for example in regenerative braking). The flow of electricity is managed through electronic power converters associated with each unit and controlled in real time.



>>> Illustration of frequency sharing of powers provided by different sources in the hybrid locomotive LHYDIE and of the power flows in a generic hybrid junction (from R. Akli, X. ROBOAM, B. Sareni).

Hybrid locomotive

We can imagine an energy management strategy based on a frequency analysis of the different power flows in a defined mission cycle. Then, through complex real-time filtering of power flows, energy management will judiciously allocate these different frequency components to the various interconnected units, based on the properties of each one. Indeed some components, such as supercapacitors, can be recharged or discharged very quickly. They can provide or absorb higher frequency components or those with high power, while others (such as fuel cells associated with their tanks, for example) are considered more as energy reserves for long-term autonomy. This approach is also illustrated by the LHYDIE hybrid locomotive power architecture (see diagram), which associates many sources with different given frequency properties. Designed in collaboration with G-ENESYS, a demonstrator of this machine is currently being developed by SNCF (French Railway). Such a "frequency sharing" method depending on the mission was developed in our research group and extended to networks onboard future aircraft or locomotives as well as to stand-alone networks supplied by renewable sources of energy.

Aircraft with fuel cells

Research studies in aviation showed that introducing hybridization in the emergency energy supply for an airliner can reduce the size of the Ram Air Turbine (wind turbine deployed as a last resort) by 30%.
The CELINA European project based on the exploratory study of the use of a fuel cell for emergency supply in aircrafts is important here too. A clever hybridization using supercapacitors can reduce the size of the fuel cell. Lastly, the projects ANR-PEPITES and MYRTE, aim to achieve energy storage in a grid-connected photovoltaic solar plant in Corsica, by producing electrolytic hydrogen.
A reversible storage set will consist of electrolyzers, fuel cells and hydrogen and oxygen tanks. The study will optimize the architecture and investigate whether hybridization by using batteries or supercapacitors is useful for energy management.

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Fuel cells for tomorrow

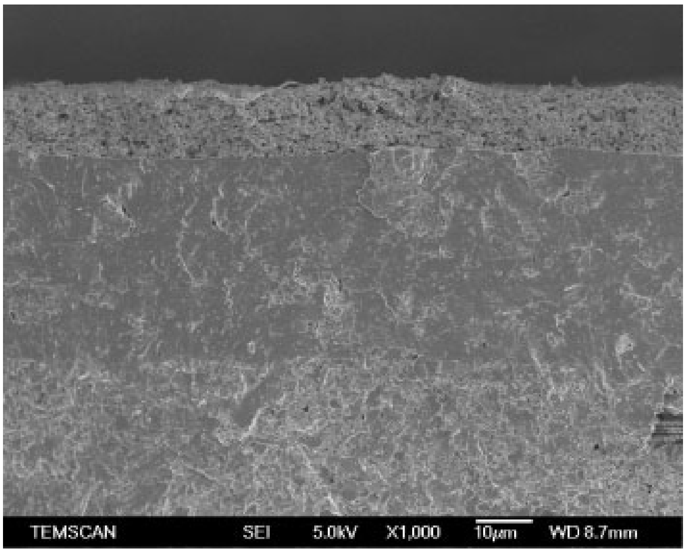
Clean and inexhaustible, the hydrogen fuel cell seems to be the ideal source of energy. At the heart of the system, a solid electrolyte solid cell (SOFC).

>>> Pierre ALPHONSE, research engineer at UPS, Florence ANSART, professor at UPS, Pascal LENORMAND, assistant professor at UPS, and Mathilde RIEU - in the CIRIMAT (joint UPS/CNRS/INP laboratory).

Will hydrogen become the renewable and unlimited fuel of the future? Only time will tell. To solve the problem of oil resources and gas shortages and reduce greenhouse effect emissions, hydrogen via fuel cells could be used in transport, to light up and heat buildings and also power computers that use fuel cells as long life batteries.

Ecological boilers

A traditional electrochemical system consumes chemical reagents to provide electricity whereas a fuel cell is an electricity (and also heat) generator that exploits the reaction between hydrogen (fuel) and oxygen (combustive element) to produce water while releasing electrons. In a cell with a solid electrolyte (Solid Oxide Fuel Cell - SOFC), the active materials are ceramics with conducting species such as O2- ions that can migrate in ceramics above 700°C. Candidates for various applications (such as micro-generation and auxiliary power units) SOFC fuel cells can be regarded as generators of the future, able to provide both electricity and heat. The main energy companies (EDF, GDF-SUEZ) are now placing their bets on SOFC technology to develop ecological boilers.



>>> Micrograph of an anode-supported SOFC mono-cell

Working tests at EDF

SOFC material requirements are numerous: concerning electrodes, a good thermomechanical and chemical stability with the electrolyte is mandatory, as well as a porous microstructure for the inlet and outlet gases -- including mixed ionic and electronic conductivity. The electrolyte must be perfectly dense and stable under oxidizing and reducing atmospheres. CIRIMAT develops several synthesis and processing methods such as the sol-gel route. Currently, in partnership with the company Saint Gobain, complete mono-cells have been manufactured at the laboratory and tested by EDF.
The high working temperature of these fuel cells (700°C-800°C) allows the use of inexpensive catalysts and the recovery of heat at temperatures interesting for cogeneration. On the other hand, high temperatures can be problematic for thermal management and mechanical resistance. If these parameters are controlled, the lifetime of the systems can be increased (approximately 20000 to 30000 hours for a prototype of 100 kW).

Technological challenge

Currently, fuel cells require hydrogen and cannot work with conventional fuels (such as hydrocarbons). However the transport and the storage of hydrogen are real technological challenges, and will probably remain so for many years to come. One way to avoid this problem involves producing a gas mixture rich in hydrogen by the reaction of steam on hydrocarbons at high temperatures -- a process called steam reforming. In this way, fuel cells can use the existing distribution network. In order to carry out this reaction in small units, CIRIMAT works on the development of microstructured catalytic reactors. These systems are based on the technology of heat exchangers manufactured by the Liebherr Aerospace company in Toulouse. Eventually this kind of exchanger will be used for the thermal coupling of the exothermic combustion of anodic effluents (with unused hydrogen) with the endothermic steam reforming reaction, which will lead to a very high energy efficiency for the complete system. The electric yield can exceed 60%. In contrast, it is only 30% for the best power generators based on thermal engines.

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The microbial fuel cell

Microbial fuel cells can treat waste and produce energy.

>>> Luc ETCHEVERRY, assistant engineer, CNRS, Marie-line DÉLIA, assistant professor at INP, Alain BERGEL, CNRS Senior Scientist and Régine Basséguy, CNRS Senior Scientist, researchers at the Laboratoire de Génie Chimique LGC (joint UPS/CNRS/INP laboratory).

>>> Benjamin ERABLE, post doctoral fellow at LGC.

Biodegradable compounds are jam-packed with energy. And what's more, some micro-organisms can convert this energy into electricity. In a microbial fuel cell, micro-organisms attached to the electrodes form an aggregate called biofilm that catalyzes the reaction of electron transfer between bio-available compounds and the electrodes. The cell can use a wide range of biomass while remaining remarkably stable.

Microbial fuel cells provide a dual function: producing electricity and cleaning up effluents by accelerating biomass degradation. The following applications are really promising: distribution of power to isolated sites, municipal and industrial effluent treatment and producing domestic electricity.

Marine battery

In a half-microbial fuel cell, micro-organisms colonize the anode and can replace minerals (platinum) needed in conventional fuel cells. They can use any kind of organic matter as fuel. For example, sugar, molasses, milk, but also other organic wastes in water treatment plants, like agricultural waste (from dairies and manure, for instance). A marine battery made from 10 individual cells has been developed at the Laboratoire de Génie Chimique (LGC-Toulouse). Each cell contains 0.5 litre of seawater and a carbon felt anode inoculated with marine micro-organisms. Using acetate as fuel, this energy-friendly system provides a power density of 5W/m^2 (current density of about 10A/m^2). This project is financially supported by the AVAMIP and received the Pollutec grand prize in 2007.

Patent pioneer

In a microbial fuel cell, microbes play the role of catalyst on both electrodes. In collaboration with the CEA, our laboratory has a pioneer patent since 2002 on this technology and continues to actively work in the domain. The team has recently developed a seawater prototype able to work using sediment organic matter or milk as fuel. A power density of about 0.3 W/m^2 was maintained over several weeks with this system, the highest value to date for equipment at sea.

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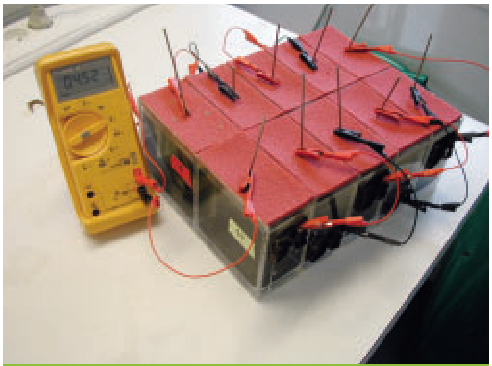


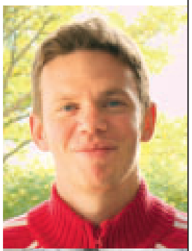
>>> Half microbial fuel with 10 cells.

Towards business creation

The Laboratoire de Génie Chimique is one of the European leaders in the development of microbial fuel cells (coordination of programmes such as European Electroactive-Biofilms, Energy ACI, ANR Bactériopile and Agri-Elec (several patents in process). Technological innovation, sustainable energy and patent generation are all strengths that help the LGC support the creation of a business project called PACMI.

Supercapacitors for storing energy?

Managing energy requires efficient stockage. Supercapacitors are an interesting alternative to lithium-ion batteries.



>>> Pierre- Louis TABERNA, CNRS research scientist and Patrice SIMON, professeur at UPS, researchers at CIRIMAT (joint UPS/CNRS/INP laboratory).

Climate change and the decreasing availability of fossil fuels means that society must move towards sustainable and renewable resources. As a result, we have seen an increase in renewable energy production from sun and wind, as well as the development of low-CO_2 emission Hybrid Electric Vehicles (HEV) and Electric Vehicles (EV). Since the sun does not shine during the night and wind does not blow exactly when we want, and the fact that we would all like to drive our cars with at least a few hours of autonomy, energy storage systems (ESS), like lead-acid, alkaline and Li-ion batteries have started to play a more important role in our lives.

Supercapacitors, also called electrical double layer capacitors (EDLC), are ESS devices akin to batteries. Somewhere between batteries and dielectric capacitors in terms of energy and power density, they can deliver higher power than batteries with less energy stored. They offer a solution to the mismatch between the fast growth in power required by devices and the inability of batteries to efficiently discharge at high rates.

Supercapacitors store charge electrostatically using reversible adsorption of ions of electrolyte onto electrochemically-stable high surface area active materials, the most common being carbon. Charge separation occurs upon polarization at the electrode/electrolyte interface. The surface storage mechanism allows very fast energy uptake/delivery and enhanced power performance compared to batteries that store charge in the bulk of the material. The mechanism explains why a supercapacitor can fully discharge in few seconds while a battery needs more than few minutes. Surface storage also allows for a very high cyclability and accordingly, supercapacitors can sustain millions of cycles while batteries survive only a few thousand at best.

Small size devices (a few farads) are widely used today for power buffer applications or for memory saving in a large variety of equipment (like toys, cameras, video recorders and mobile phones). Cordless tools like screwdrivers and electric cutters using EDLCs are already on the market, using devices of a few tens of farads. The main application targeted by manufacturers over the next few years is transportation, with the HEV, where supercapacitors will be used to deliver high power density for a few seconds (boost) but they will also be able to recover braking energy (power uptake). Several train manufacturers (including Bombardier and Alstom) have clearly identified the tramway/metro market segment as extremely relevant for EC use, for train powering over small distances in city centres (where electric cables are clearly undesirable for aesthetic reasons) but also for recovering the braking energy of another train on the same line thanks to their symmetric high power delivery/uptake characteristics.

>>> A supercapacitor integrated into a crane.

Nanoporous carbon for supercapacitors

At CIRIMAT, work on supercapacitors is mainly focused on the development of new carbon materials with optimized properties for energy storage. As previously mentioned, unlike traditional batteries, which store electricity chemically, supercapacitors store electricity electrostatically by physically separating positive and negative charges along two electrical conductors: electrolyte ions and high surface area carbon electrodes (1000-2000 m^2g^{-1}). Such high surface areas are achieved through an activation treatment involving a partial, controlled oxidation of the carbon, which leads to a porous network developing inside the carbon grains. This results in an enhancement of the material's ability to store charges.

It was previously thought that reducing the carbon pore size below one nanometre would destroy its storage capacity because ions would not penetrate into these small pores. We have turned this old idea on its head by proving that smaller, lighter and more powerful supercapacitors could be developed by using pores smaller than one nanometre. As a result of a collaboration with Drexel University (Philadelphia, US), we were able to design tailored pore sizes in carbon ranging from 0.6 to 1.2 nanometres, by using carbide-derived carbon (CDC). Surprisingly, we found that carbon with 0.7 nm pores increased the amount of stored energy by about 100%, an effect explained by the deformation of the solvent molecule's shell surrounding the ion. Recent work has confirmed these results and shown that the optimum pore size for adsorption in these confined pores is close to the bare ion size. These results are interesting at different levels. First, from an applications point of view, they offer new ways of designing high-energy density supercapacitors, with a energy density close to 10 Wh/kg. From a fundamental point of view, they rule out the generally accepted description of the double layer (solvated ions adsorbed on both sides of the pore walls) in these sub-nanometre pores.

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